FeNₓ/C catalyst is one of the most promising non-precious electrocatalyst for oxygen reduction reaction (ORR) applied in fuel cells. This catalyst is derived from high-temperature pyrolysis of the mixture of common N-containing species, inorganic iron salt, and carbon black, so has very low cost. Currently, the ORR performance of advanced FeNₓ/C is close to that of Pt catalyst even in acidic solution. However, there is one open question: what is the active site structure? The addition of iron salts is vital for improving the ORR activity. However, some opinions insist that iron only plays the role for the formation of catalytic active sites, but does not directly act as active sites.

Herein, we prepared a high active FeNₓ/C catalyst derived from poly-m-phenylenediamine (poly-m-PDA). To probe the active sites, especially to determine whether active site contain iron, we investigated a series of small molecules and ions on the ORR performance of the FeNₓ/C catalyst. It was found that SCN⁻ ion can greatly suppress the ORR activity in acidic solution, and high concentration of Cl⁻ ion (e.g., 1 M) also has the same effect. This result indicates the active site of FeNₓ/C should contain iron atoms. We further compared the poisoning effect of these additives on ORR performance in both acidic and alkaline solution. It was found that in alkaline solution, the FeNₓ/C has a much higher tolerance for contaminants than that in acidic solution. For example, in high concentration of NaCl solution (e.g., 0.1 M NaOH + 1 M NaCl), the ORR activity is even better than that in the blank solution (0.1 M NaOH). However, high concentration of NaSCN still can poison the FeNₓ/C catalyst for ORR. This result suggest that in alkaline solution, the active site of the FeNₓ/C catalyst still contain iron atom, but may combine with OH. As a result, weak ligand (e.g., Cl⁻) to iron can not poison the catalyst, while strong ligand (e.g., SCN⁻) still can suppress the ORR performance through replacing with OH and occupying the iron site.